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Publication date:
2019

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):
Birch, H., Trac, N. L., & Mayer, P. (2019). *Partitioning based determinations of water solubility for volatile hydrophobic liquid chemicals*. Poster session presented at SETAC Europe 29th annual meeting, Helsinki, Finland.

This study was funded by:

Partitioning based determinations of water solubility for volatile hydrophobic liquid chemicals

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Introduction

Water solubility is experimentally and analytically challenging to determine for volatile hydrophobic liquid chemicals, because they are prone to the formation of micro-droplets and emulsions in water and are easily lost from water.

Earlier studies showed that direct passive dosing (DPD) from 90% loaded silicone agreed with headspace passive dosing (HPD) measurements, while DPD from 100% loaded silicone produced markedly higher concentrations (third phase).[1]

Aim

The aim of this study was to investigate and optimize the two partitioning based methods for solubility testing of hydrophobic liquid chemicals by:

1) Determining equilibration kinetics for the HPD system
2) Measuring the chemical activity above a high capacity lipid donor
3) Approaching solubility and maximum activity from below, using a series of dilutions in miglyol for HPD and varying loading of the silicone for DPD.

Methods

1. Headspace passive dosing kinetics

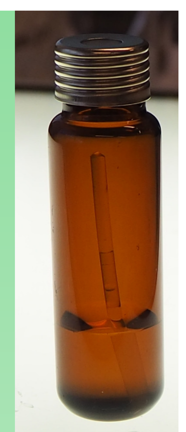
- Glass inserts with glass wool were placed in 20 mL vials and left overnight at 20°C
- 5.5 mL MilliQ water was added to each vials
- A mixture of liquid test chemicals was added to the inserts ((+)-α-pinene, *n*-decane, *trans*-decalin, 1,3,5-triethylbenzene, hexylcyclohexane, isopropyl myristate, and dodecylbenzene)
- Vials were shaken at 100 rpm, 10 mm orbit (no movement of the insert) for 0.3-24 hours
- Analysis: headspace SPME and GC-MS

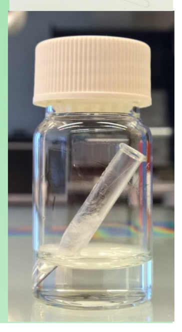
2. Chemical activity above a lipid donor

- Binary mixtures of (+)-α-pinene or nonane with miglyol from 1-100 weight% test chemical were prepared in 20 mL headspace vials
- Analysis: headspace sampling (syringe) and GC-MS
- Peak areas were normalized to measurements above the pure phase liquid chemical

3. Approaching solubility

- Cleaned silicone rod (d: 3mm) was cut into pieces of 0.3 or 0.4 g
- Immersion in liquid test chemical for ½-24 hours produced varying loadings of rods. Loaded rods were wiped with damp lint free tissue and rinsed minimum three times with MilliQ water
- The loaded rods were equilibrated with MilliQ water by rolling at 20 rpm for 2 hours
- Headspace dosing systems were prepared (see 1) and binary mixtures of dodecylbenzene, decane, hexylcyclohexane or (+)-α-pinene with miglyol from ~40-100 vol% were added to the inserts. Test systems were shaken for 7 hours.
- Analysis: liquid/liquid extraction (2.5 mL iso-octane to 2.5 mL sample) and GC-MS. ^{13}C-labeled served as internal standard for dodecylbenzene and naphthalene for hexylcyclohexane.





Headspace passive dosing kinetics

Equilibrium times, $t_{95\%}$, were 2-6 hours for five chemicals with log K_{ow} of 4-6 and K_{aw} of 0.8-200.

Highly varying results were seen for chemicals with a log Kow >6 that are most prone to the formation of micro-droplets.

A prolonged temperature equilibration of all materials reduced this issue (Figure 3, dodecylbenzene).

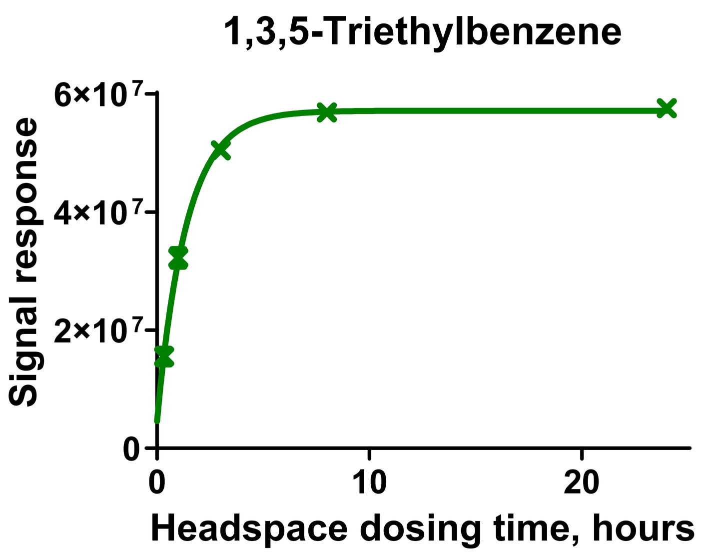


Figure 1: Headspace dosing kinetics for 1,3,5-triethylbenzene. n=3, error bars: SEM.

Chemical activity

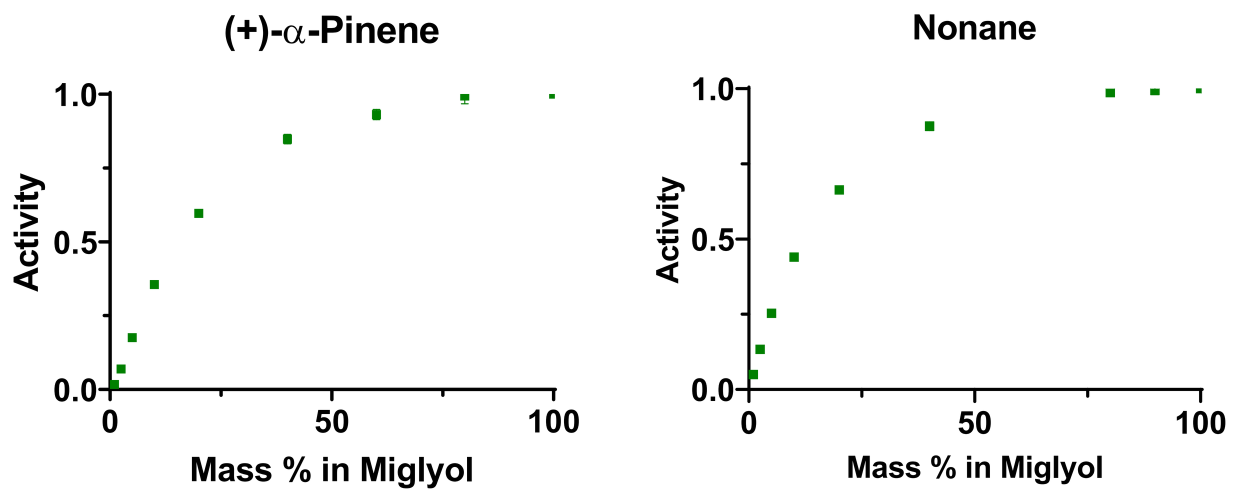


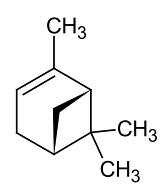
Figure 2: Chemical activity of (+)-α-pinene (left) and nonane (right) measured above their binary mixtures in miglyol.

Experiences and findings

- Careful temperature equilibration of all materials is important to avoid condensation of test chemical during equilibration.
- Precision of headspace passive dosing was confirmed by measurements at and slightly below saturation.
- Both methods worked for (+)-α-pinene (lowest hydrophobicity)
- Oversaturation of water was seen for direct passive dosing of highly hydrophobic chemicals.
- Accuracy of the fast headspace passive dosing method was confirmed by the more established slow stir method.

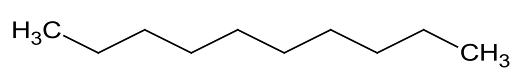
Approaching solubility

(+)-α-Pinene



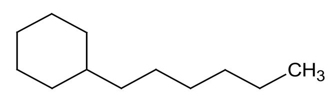
logK_{ow}: 4.44

***n*-Decane**



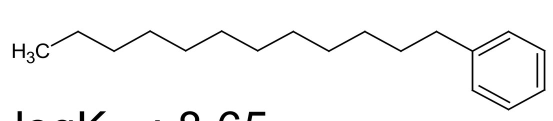
logK_{ow}: 5.01

Hexylcyclohexane



logK_{ow}: 6.05

Dodecylbenzene



logK_{ow}: 8.65

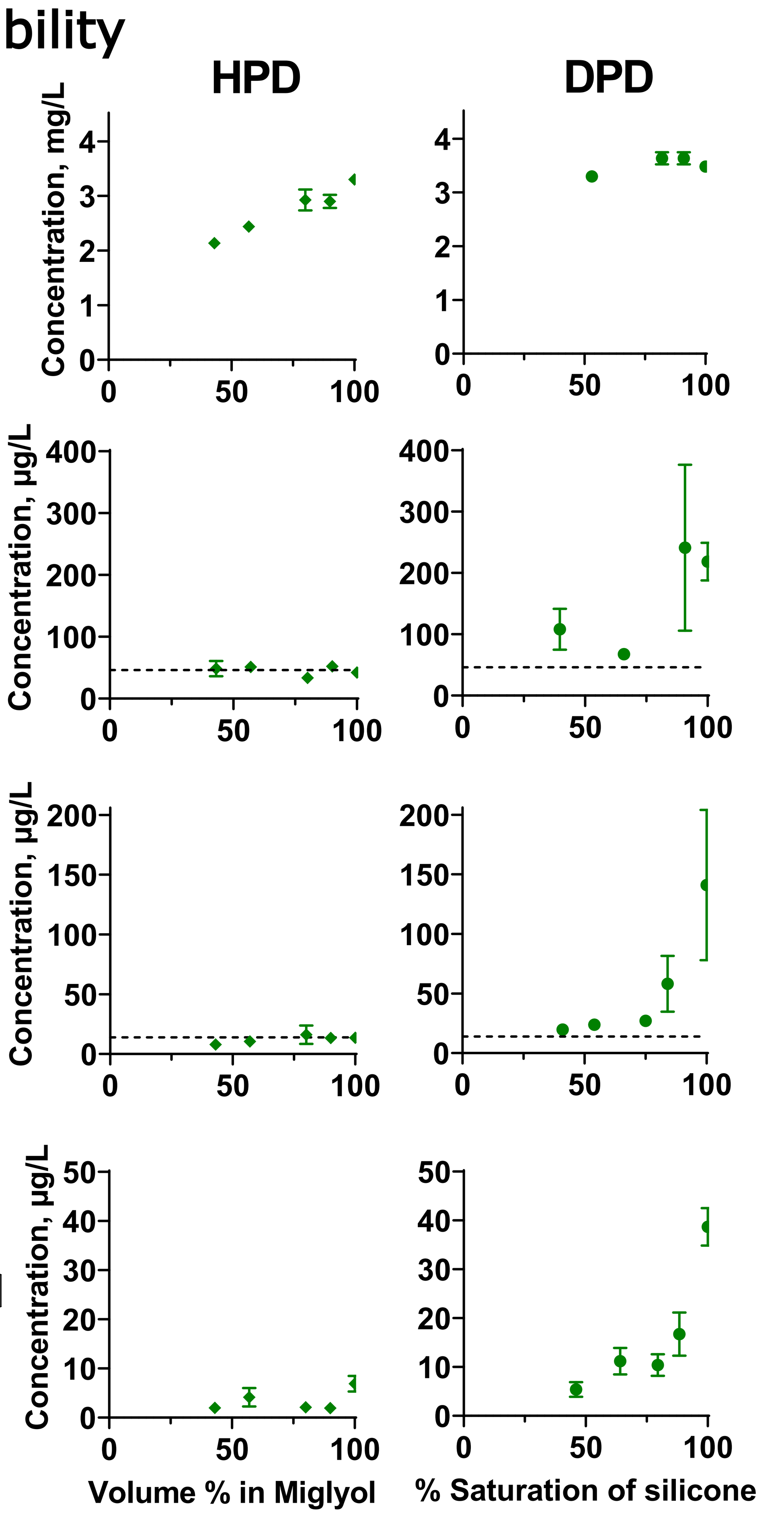


Figure 3: Headspace passive dosing from binary mixtures in miglyol (left) and direct passive dosing from partly to fully saturated silicone rods (right). Dashed lines for decane and hexylcyclohexane indicates literature solubility[2] and consensus solubility from a mini-ring test (5 labs) using the slow stir method[3]. Three outliers (one for hexylcyclohexane and two for dodecylbenzene) > 5 times higher than both other replicates were removed.

Acknowledgements: We thank Hanne Bøggild for technical assistance and Dan Letinski, Aaron Redman and the Cefic LRI Research Liaison Team for input and discussions.

[1]Birch, H., Trac, L.N., Mayer, P. 2018. New approaches for determining solubility of volatile liquid chemicals, Poster MO436, SETAC Europe 13-17th May 2018, Rome, Italy.

[2]Tolls, J., Van Dijk, J., Verbruggen, E.J.M., Hermens, J.L.M., Loeprecht, B., Schüürmann, G., 2002. Journal of Physical Chemistry A, 106: 2760-2765.

[3]Letinski, D., Birch, H., Redman, A., Mayer, P., Dolich, T., Lanzinger, A., Lange, J., MacKenzie, C.E., Thomas, D. 2019. Water solubility methods mini-ring test. Deliverable D2.1, Cefic LRI-Eco38 project.